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Temporal trends for inflow of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) to Tokyo Bay, Japan, estimated by a receptor-oriented approach

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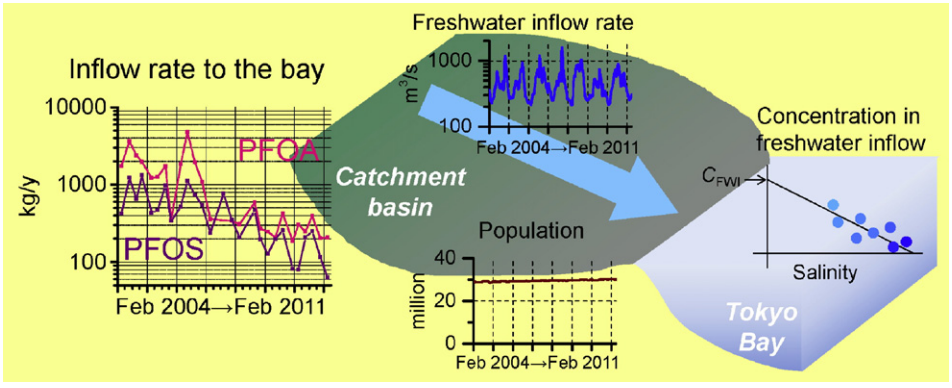
HIGHLIGHTS

- Inflow rates of PFOS and PFOA to Tokyo Bay, Japan, were estimated.
- A receptor-oriented approach was based on sampling of the bay water.
- Their inflow rates decreased from February 2004 to February 2011 in differing ways.
- The decreases likely reflected emission reductions in the catchment basin.

GRAPHICAL ABSTRACT



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ABSTRACT

We estimated inflow rates of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) to Tokyo Bay, Japan, between February 2004 and February 2011 by a receptor-oriented approach based on quarterly samplings of the bay water. Temporal trends in these inflow rates are an important basis for evaluating changes in PFOS and PFOA emissions in the Tokyo Bay catchment basin. A mixing model estimated the average concentrations of these compounds in the freshwater inflow to the bay, which were then multiplied by estimated freshwater inflow rates to obtain the inflow rates of these compounds. The receptor-oriented approach enabled us to comprehensively cover inflow to the bay, including inflow via direct discharge to the bay. On a logarithmic basis, the rate of inflow for PFOS decreased gradually, particularly after 2006, whereas that for PFOA exhibited a marked stepwise decrease from 2006 to 2007. The rate of inflow for PFOS decreased from 730 kg/y during 2004–2006 to 160 kg/y

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Inflow rate
Surface water
Catchment basin
Receptor-oriented analysis
Emission source

in 2010, whereas that for PFOA decreased from 2000 kg/y during 2004–2006 to 290 kg/y in 2010. These reductions probably reflected reductions in the use and emission of these compounds and their precursors in the Tokyo Bay catchment basin. Our estimated per-person inflow rates (i.e., inflow rates divided by the estimated population in the basin) for PFOS were generally comparable to previously reported per-person waterborne emission rates in Japan and other countries, whereas those for PFOA were generally higher than previously reported per-person waterborne emission rates. A comparison with previous estimates of household emission rates of these compounds suggested that our inflow estimates included a considerable contribution from point industrial sources.

1. Introduction

Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are two of the most widely detected perfluoroalkyl substances in the environment, and they are emitted to the environment through human activities (Giesy and Kannan, 2002; Lau et al., 2007; Paul et al., 2009; Prevedouros et al., 2006). These compounds are a focus of worldwide concern (United Nations, 2009) because of their persistence in the environment (Giesy and Kannan, 2001; Giesy and Kannan, 2002; Houde et al., 2011; Sakurai et al., 2010), their retention in the human body (Olsen et al., 2007), and their toxicities (Ankley et al., 2004; Giesy and Kannan, 2002; Hekster et al., 2003).

Regulations on the production and use of PFOS and PFOA have been introduced in Japan and elsewhere in recent years, and emission rates of these compounds may have declined in response. PFOS was added to the Stockholm Convention on Persistent Organic Pollutants list (in Annex B) in 2009 (United Nations, 2009), which obliged ratifying nations to restrict its production and use. In Japan, the production and use of PFOS have been restricted by several laws. In April 2010, in response to its listing under the Stockholm Convention, PFOS was added to the list of "Class I Specified Chemical Substances" of Japan's Chemical Substances Control Law (CSCL), making it one of the nation's most strictly regulated chemicals. Major PFOA producing companies have joined a stewardship program of the U.S. Environmental Protection Agency in which they voluntarily committed to reduce emissions of PFOA and related compounds by 95% (compared with the emissions in 2000) by 2010 and by 100% by 2015 (U.S. Environmental Protection Agency, 2006). Under Japan's CSCL, PFOA is classified as one of the "General Chemical Substances", and the annual amount manufactured or imported by a company must be reported to the government if it equals or exceeds 1 tonne.

Temporal trends in the inflow rates of PFOS and PFOA to a water body are an important basis for evaluating changes in their emission on a regional scale, but reports of such trends are scarce. Measurements of PFOS and PFOA concentrations in river water and effluent from wastewater treatment plants (WWTPs) have been used to estimate inflows of PFOS and PFOA (Becker et al., 2008; Huset et al., 2008; Kim, 2012; Kim et al., 2014; Murakami et al., 2008; Murakami et al., 2009; Pistocchi and Loos, 2009; Schultz et al., 2006; Sinclair and Kannan, 2006; Takazawa et al., 2009; Zushi et al., 2011). The relatively low vapor pressures and high water solubilities of these ionic compounds (Giesy and Kannan, 2002; Prevedouros et al., 2006) suggest that surface water is an appropriate medium to monitor their waterborne emissions (i.e., their discharge as wastewater effluent or discharge to sewage or water bodies). Thus, inflow estimates based on measurements of PFOS and PFOA concentrations should reflect actual regional waterborne emissions and would complement emission estimates based on production and commercial records (Paul et al., 2009; Prevedouros et al., 2006). However, the available inflow estimates were made on the basis of one-time sampling campaigns and were not intended to provide temporal trends.

In the present study we estimated temporal trends for inflow rates of PFOS and PFOA to Tokyo Bay, Japan, between February 2004 and February 2011, using a receptor-oriented approach based on field samplings of the bay water. Tokyo Bay (Fig. 1) is highly impacted by anthropogenic activities, given that its catchment basin is one of the world's most populous areas (Sakurai et al., 2000; Sakurai et al., 2010), and the inflow of these anthropogenic compounds from the catchment basin to the bay is of interest. Previously, we ascertained the three-dimensional distributions of these compounds in the bay and proposed a simple mixing model for estimating their average concentrations in the freshwater inflow to the bay based on their measured concentrations in the bay (Sakurai et al., 2010). Here, we applied this model to estimate the PFOS and PFOA concentrations in the freshwater inflow to the bay corresponding to the samples collected during each sampling campaign conducted four times a year. The estimated concentrations were multiplied by estimated rates of freshwater inflow to yield the mass rates of inflow of PFOS and PFOA to the bay, which approximate the waterborne emissions of these compounds in the Tokyo Bay catchment basin. We divided the estimated inflow rates by the estimated population in the catchment basin to obtain per-person inflow rates, and compared the results with estimates from previous studies. Our comprehensive receptor-oriented method also enabled us to discuss

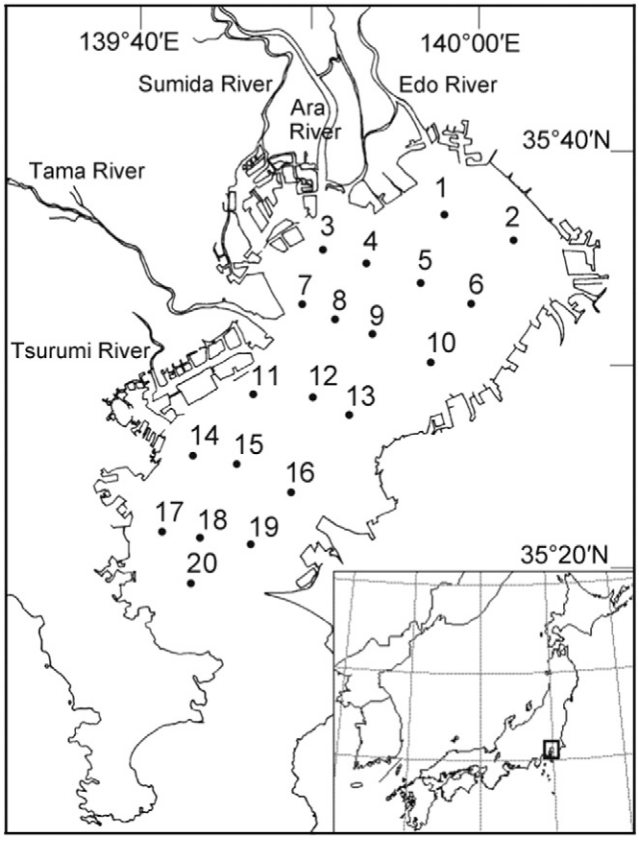

Fig. 1. Tokyo Bay and locations of sampling stations (coordinates given by Sakurai et al. (2010)). The nominal position of station 7 was changed to 35.5600 °N, 139.8433 °E (approximately 2 km northeast of its previous position) after the May 2007 sampling.

the relative contributions of point industrial sources and diffuse household sources. The water system of the Tokyo Bay catchment basin is complicated by diversion weirs in major rivers, water intake from outside the catchment basin, and flood management during high precipitation events, and these factors were carefully considered in our estimates of the inflow of these compounds.

2. Materials and methods

2.1. Sampling

Water samples for the present study were collected on a quarterly basis in Tokyo Bay at 10% and 90% of the water depth at stations 1–20 in February 2007 and at stations 6, 7, 12 and 17 after February 2007 (Fig. 1). To the resulting data set we added concentration and salinity data obtained from quarterly sampling at the same 20 stations and depths during 2004–2006 (Sakurai et al., 2010). Tokyo Bay lies southeast of Tokyo metropolitan area and opens to the Pacific Ocean on the south. Its catchment basin is densely inhabited (>2000 persons/km^2) and encompasses a wide variety of municipal, agricultural, and industrial activities, including an active fishery in the bay itself. The sampling program was established previously to cover Tokyo Bay horizontally and vertically (Sakurai et al., 2010). We chose four of these sampling stations after February 2007 on the basis of relatively high concentrations and a wide range of salinity observed during the preceding period (2004–2006) (Sakurai et al., 2010) to enable effective application of the mixing model. One-day sampling campaigns were conducted using two boats on the following dates: 22 February, 16 May, 8 August, and 14 November 2007; 20 February, 15 May, 25 August, and 5 November 2008; 4 February, 10 May, 9 August, and 9 December 2009; 17 February, 16 May, 9 August, and 17 November 2010; and 16 February 2011. Water samples measuring 1 L or more were collected during daytime, generally within a period of 7 h. Collection, transport, and storage of the samples were performed as previously described by Sakurai et al. (2010), with the exception that solvent-rinsed polypropylene bottles were used as sample containers after February 2007 instead of glass bottles. Salinity was recorded at both sampling depths at each station with a conductivity, temperature, and depth profiler.

2.2. Chemical analysis

Determination of the concentrations of PFOS and PFOA in the water samples (sum of dissolved and particulate phases) essentially followed previously reported methods (Sakurai et al., 2013; Sakurai et al., 2010). Briefly, a 100-mL aliquot of each sample was filtered through a precombusted glass-fiber filter. The methanol extract of the freeze-dried filter was obtained by sonication and centrifuged, and the supernatant was concentrated. The filtrate and the concentrated supernatant were combined, spiked with ^{13}C-labeled surrogate compounds, and then purified by using a C18 solid-phase extraction cartridge. The eluate from the cartridge was concentrated and finally dissolved in 500 μL of 1:1 (*v*/*v*) methanol in Milli-Q water. For some samples, concentrations in the dissolved and particulate phases were determined separately, by using a 500-mL aliquot of each sample. The filtrate and filter were each spiked with the surrogate compounds, and then separately extracted and purified similarly as described above. PFOS and PFOA were identified and quantified by injecting an aliquot of the final concentrated extract into a liquid chromatograph (C18 column) connected to a triple–quadrupole-type tandem mass spectrometer. Quantification was based on the isotope dilution method. Details of the data quality assurance and control are described in the Supporting Material (SM). Detection limits were determined based on a signal-to-noise ratio of 8 on chromatograms and three times the standard deviation of the method blank values, or based on the variability of seven repeated analyses of a composite seawater sample, depending on the periods of sample collection. The method blank was determined by analyzing one or two blank samples (Milli-Q water) for each sampling campaign, and the average blank value, if detected, was subtracted from measured concentrations in the samples. The blank during the sampling campaign was evaluated by a combination of sampling blanks and travel blanks, and was considered negligible because the sampling blanks (Sakurai et al., 2010) and travel blanks were not detected. Concentrations above the detection limits were quantified. A value of half the detection limit was assigned to values below the detection limits.

2.3. Estimating concentrations in the freshwater inflow

The mixing model (Eq. (1)) proposed in the previous study (Sakurai et al., 2010) was adopted to estimate the concentrations of PFOS and PFOA in the freshwater inflow to the bay. In the present study, freshwater inflow was defined to include all forms of freshwater flowing into Tokyo Bay (e.g., river discharge, effluent from WWTPs, and direct discharge from coastal industrial facilities) and precipitation on the bay surface.

$$C = \alpha_{FWI} C_{FWI} + \alpha_{ocean} C_{ocean} \quad (1)$$

In Eq. (1), C is the concentration of PFOS or PFOA in each sample, C_{FWI} is the average concentration of the compounds in the freshwater flowing into the bay, C_{ocean} is the average concentration of the compounds in Pacific Ocean water, and α_{FWI} and α_{ocean} are the relative contributions of fresh water and ocean water to the water sample, respectively ($\alpha_{FWI} + \alpha_{ocean} = 1$). The salinity of each sample (S) divided by the salinity of Pacific Ocean seawater (S_{ocean}) was used as α_{ocean}. S_{ocean} was set to 35.5 (Sakurai et al., 2010).

The value of C_{FWI} was calculated by applying Eq. (1) to each sample, using the measured values of C and S, and we used the Hodges–Lehmann estimator (Hollander and Wolfe, 1999), a rank-based distribution-free estimator of the central tendency of a population, as the representative value of C_{FWI} ($\hat{C}_{FWI}$) for each sampling campaign, along with the associated 95% confidence interval (CI). Some data were omitted in the calculation because corresponding salinity data were not available. For data from the February 2008 campaign, an 87% CI was calculated because the small number of salinity data ($n = 4$) precluded the calculation of a 95% CI. The value of C_{ocean} was set at 55 pg/L for PFOS and 380 pg/L for PFOA (Yamashita et al., 2005). For confirmation, $\hat{C}_{FWI}$ was also estimated by weighted least-squares (WLS) regression of Eq. (2) by using $\hat{C}^{-2}$ as the weight ($\hat{C}$ is an estimate of C). Eq. (2) was derived from Eq. (1) by setting C_{FWI} to a_0 and ($C_{ocean} - C_{FWI}$) / S_{ocean} to a_1. $\hat{C}_{FWI}$ was obtained by setting $S = 0$ in Eq. (2) after the regression.

$$C = a_0 + a_1 S \quad (2)$$

2.4. Rate of freshwater inflow to Tokyo Bay

The rate of freshwater inflow to Tokyo Bay was estimated based on a regression equation (Eq. (6), Section 3.3) established between the monthly averages ($\overline{q}_{FWI}$) of the freshwater inflow rate to Tokyo Bay (Okada et al., 2007) and monthly averages ($\overline{q}_{TR}$) of the daily flow rate of the Tone River at the Tone-Ohzeki diversion weir (q_{TR}) (provided by the Japan Water Agency) between July 2002 and June 2003. The weighted average of q_{TR} for the 50 days prior to each sampling date ($\hat{q}_{TR}$) was used as a representative value for q_{TR} on sampling date t to account for the impact of PFOS and PFOA that had flowed into the bay prior to the sampling date (Eq. (3)).

$$\hat{q}_{TR}(t) = \sum_{j=t-T}^{t} [q_{TR}(j)\, w(j)] / \sum_{j=t-T}^{t} w(j) \quad (3)$$

where $T = 49$ and w is the weight, which assumed an exponential decrease of the impact. The averaging period was set at 50 days to account

for a contribution as small as about 1% from each $q_{TR}(j)$ to $\hat{q}_{TR}$. The weight was calculated by Eq. (4).

$$w(j) = \prod_{i=j}^{t} d(i), \quad d(i) = \exp\left[-\tau(i)^{-1}\right] \ (i<t), \quad d(i) = 1 \ (i = t) \qquad (4)$$

where τ is the residence time of water in Tokyo Bay estimated for each month of the year (range, 16–46 days) (Okada et al., 2007). Eq. (6) was then used to estimate a representative value $\hat{q}_{FWI}$ for each sampling date based on $\hat{q}_{TR}$.

2.5. Population in the Tokyo Bay catchment basin

The boundary of the Tokyo Bay catchment basin (Ministry of Land, Infrastructure and Transport, 2007; Miyamura, 1993) was defined on a GIS-based system based on the catchment basins of segments of rivers defined in previous studies (Suzuki et al., 2005; Suzuki et al., 2004). The coastal part of the basin was defined in this system in the present study. The Tokyo-Bay catchment basin was divided into five sub-catchment basins (Fig. 2). In addition, the populations in the catchment basins of the water intake sites at the Sakawa and Sagami Rivers were considered. These rivers run outside the Tokyo-Bay catchment basin, but some of their water was transported across the basin boundary (Okada et al., 2007).

The population in each sub-catchment basin was estimated by linear interpolation or extrapolation of the 2000, 2005, and 2010 national census values. Population was calculated based on census results, as allocated to grid squares of 0.5 min of latitude and 0.75 min of longitude (about 1 km × 1 km in the study area) (Grid Square Statistics, Statistics Bureau, Ministry of Internal Affairs and Communication, Japan). When parts of the grid square were outside the boundary, the population in that square was allocated to the catchment basin based on relative areas in the boundary.

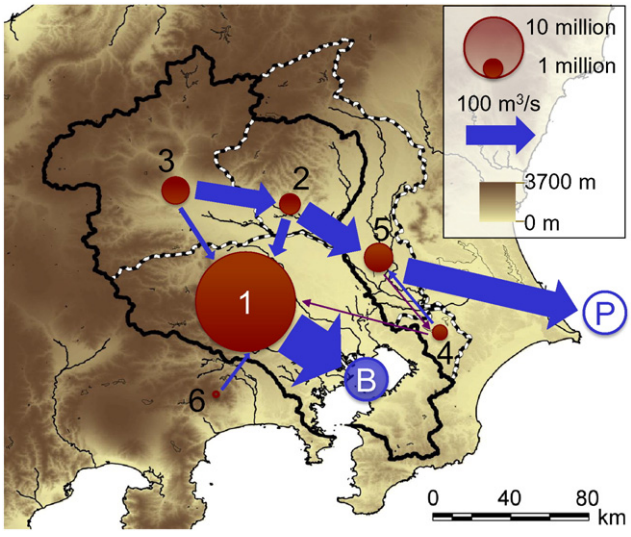

Fig. 2. Schematic representation of six sub-catchment basins included in the calculation of the effective population in the Tokyo Bay catchment basin. Blue arrows show normal flow of water to Tokyo Bay (B) and the Pacific Ocean (P), with their widths representing their rates. Circles with numbers represent sub-basins, with their areas representing their populations. Precipitation in sub-basin 1 flows exclusively into Tokyo Bay. Sub-basin 2 is the catchment basin of the Tone River from the Tone-Ohzeki weir to the Sekiyado distributary point to the Edo River, and sub-basin 3 is that of the Tone River upstream of the Tone-Ohzeki weir. Sub-basins 2 and 3 provide water to the Tokyo Bay catchment basin via the water intake at the Tone-Ohzeki weir or the distributary to the Edo River. Sub-basin 4 is the catchment basin of Imbanuma Lake. Sub-basin 5 is the catchment basin of the Tone River from the Sekiyado distributary point to the confluence from Imbanuma Lake. Sub-basins 4 and 5 provide water to the Tokyo Bay catchment basin only when the water level in the Tone River is high and a pumping station diverts its water to Tokyo Bay through the Imbanuma Lake channel (purple arrows; note that these are enlarged for visibility). Sub-basin 6 comprises the catchment basins of the water intake sites of the Sagami and Sakawa Rivers and is outside the Tokyo Bay catchment basin. The Tokyo Bay catchment basin as defined in the present study (sub-basins 1–3) is outlined with a bold black line, and sub-basins 1–5 are outlined with a broken line.

Finally, the effective population in the Tokyo Bay catchment basin was determined by taking into account the water intake and distributary inflow from outside the catchment basin. The main stream of the Tone River does not flow into Tokyo Bay, but it provides a considerable flow of water (roughly one-third of $\hat{q}_{FWI}$ on average) into the Tokyo Bay catchment basin via water intake and distributary outflow (Fig. 2). The effective population in the basin thus was calculated by adding the population above the weir or distributary point multiplied by the water intake ratio (Fig. S1, SM). Water intake at the Tone-Ohzeki weir, distributary flow to the Edo River, and water diverted through the Imbanuma Lake channel were estimated by using daily flow data provided by the pertinent management authority (the Japan Water Agency or Ministry of Land, Infrastructure, Transport and Tourism) (Fig. 2). The effective population associated with water intake from the Sakawa and Sagami Rivers was calculated similarly. Other details of this calculation are in SM Table S1. Daily estimates of the effective population in the Tokyo-Bay catchment basin were weighted averaged to obtain the representative effective population ($\hat{N}_e$) at the date of each sampling campaign. Averaging was performed as described for $\hat{q}_{TR}$.

2.6. Inflow estimates of PFOS and PFOA to Tokyo Bay

The basin-wide inflow rate from the catchment basin of the bay (I_{basin}) was estimated as $I_{basin} = \hat{C}_{FWI} \times \hat{q}_{FWI}$ for each sampling campaign. The corresponding per-person inflow rate (I_{pp}) was estimated as $I_{pp} = I_{basin}/\hat{N}_e$.

The combined uncertainties in these estimates were assessed based on propagation of the uncertainties in the measured concentrations, those in the other data, and those introduced at each step of calculation (Hoff, 1994; Joint Committee for Guides in Metrology, 2008). The expanded relative uncertainty (E) was obtained from combined relative standard uncertainties (ε) by using a coverage factor k, which was set to 2 (Joint Committee for Guides in Metrology, 2008). For example, $E(I_{pp})$ was obtained by Eq. (5).

$$E(I_{pp}) = k\varepsilon(I_{pp}) = k\sqrt{\varepsilon\left(\hat{C}_{FWI}\right)^2 + \varepsilon(\hat{q}_{FWI})^2 + \varepsilon\left(\hat{N}_e\right)^2} \qquad (5)$$

Relative uncertainties were assigned to the parameters based on previous studies and the authors' judgment (SM Table S2). The details of the method of uncertainty analysis are provided in the SM.

The seasonal correlation between the PFOS or PFOA inflow rate and the freshwater inflow rate was assessed by Pearson's correlation coefficient between the logarithm of the normalized inflow rate of the compound and the logarithm of the freshwater inflow rate ($\hat{q}_{FWI}$). The inflow rates for PFOS or PFOA were divided by their annual maxima (the February 2011 datum was treated as 2010 data) to derive normalized values. The 95% CIs of the population correlation coefficients were estimated by Fisher's z transformation. 95% CIs are indicated in square brackets. Statistical analyses were carried out with Microsoft Excel (Version 14, Microsoft, Redmond, WA, USA), IBM SPSS Statistics (Version 21, International Business Machines Corp., Armonk, NY, USA), and StatXact (Version 8, Cytel Inc., Cambridge, MA, USA).

3. Results and discussion

3.1. Concentrations of PFOS and PFOA in Tokyo Bay water

Whereas no temporal trends were reported in the concentrations of PFOS and PFOA in Tokyo Bay water during 2004–2006 (Sakurai et al., 2010), after 2006 the PFOS and PFOA concentrations observed at

stations 6, 7, 12, and 17 tended to decrease with time (SM Fig. S2). Concentrations were not available for PFOS in May 2007 and May 2008 or for PFOA in May and August 2007 and May 2008 due to problems encountered in the chemical analysis. Salinity data were missing for stations 1–10 in the February 2008 sampling.

3.2. Average concentrations of PFOS and PFOA in freshwater inflow ($\hat{C}_{FWI}$)

A strong correlation between salinity and concentration of PFOS or PFOA was generally observed for each sampling campaign (SM Fig. S3), supporting the validity of the mixing model (Eq. (1)). The temporal trend for $\hat{C}_{FWI}$ (Fig. 3A) was similar to the overall trend for the concentration in the bay, which decreased after 2006. On a logarithmic scale, the PFOS concentration decreased gradually, whereas the PFOA concentration decreased stepwise from 2006 to 2007. The median of $\hat{C}_{FWI}$ for PFOS decreased from 45 ng/L in 2004–2006 to 10 ng/L in 2010, whereas that for PFOA decreased from 110 ng/L in 2004–2006 to 14 ng/L in 2010. The estimated $\hat{C}_{FWI}$ values obtained from the present method and the WLS regression were comparable (SM Fig. S4).

3.3. Rate of freshwater inflow to Tokyo Bay

Data for the monthly rate of freshwater inflow to Tokyo Bay ($\overline{q}_{FWI}$) were fit by regression Eq. (6) (SM Fig. S5).

$$\overline{q}_{FWI} = 2.50\,[2.16{-}2.87]\,\overline{q}_{TR} \tag{6}$$

The estimated $\hat{q}_{FWI}$ fluctuated seasonally (SM Fig. S6) in accordance with the normal precipitation pattern in this region of Japan. The median, minimum, and maximum of the $\hat{q}_{FWI}$ values for the 29 sampling campaigns (including the two for which both PFOS and PFOA data were not available) were 435, 227, and 1070 m^3/s, respectively.

3.4. Population in the Tokyo Bay catchment basin

The representative effective population in the basin ($\hat{N}_e$) increased slowly (0.0015%/y on average) from 19 February 2004 to 16 February 2011, with small fluctuation due to changes in water intake (SM Fig. S7). The median, minimum, and maximum values of $\hat{N}_e$ for the 29 samplings were 29.5 million, 28.5 million, and 30.1 million, respectively.

3.5. Temporal trends in the inflow rates of PFOS and PFOA to Tokyo Bay

The overall temporal trends in the inflow rates of PFOS and PFOA from the Tokyo Bay catchment basin (I_{basin}) (Fig. 3B) were similar to that for $\hat{C}_{FWI}$. Values of I_{basin} for PFOS decreased gradually on a logarithmic scale, particularly after 2006; the yearly average decreased from 730 kg/y during 2004–2006 to 160 kg/y in 2010. Values of I_{basin} for PFOA showed a marked stepwise decrease from 2006 to 2007, averaging 2000 kg/y during 2004–2006 and 290 kg/y in 2010. The temporal trends in the per-person inflow rates (I_{pp}) of these compounds were identical to those for I_{basin} because the population in the basin was virtually constant. The yearly average of I_{pp} for PFOS decreased from 69 μg/d during 2004–2006 to 15 μg/d in 2010, and that of I_{pp} for PFOA decreased from 190 μg/d during 2004–2006 to 26 μg/d in 2010 (Table 1). The seasonal pattern for the PFOS inflow rate was similar to that for $\hat{q}_{FWI}$, whereas the seasonal pattern for the PFOA inflow rate was less clear. The year-normalized inflow rate for PFOS was strongly correlated with $\hat{q}_{FWI}$ (correlation coefficient 0.86 [0.72–0.94], $n = 27$), whereas the correlation of PFOA with $\hat{q}_{FWI}$ was weaker and not statistically significant (0.32 [−0.075 to 0.63], $n = 26$).

The considerable reduction in the inflow rates of PFOS and PFOA to Tokyo Bay between February 2004 and February 2011 (Fig. 3B and Table 1) probably reflected a reduction in the use and emission of these compounds and their precursors in the Tokyo Bay catchment basin. The reduction in inflow rates accorded with reduced concentrations of PFOS and PFOA reported in the Tama River, a major river flowing into Tokyo Bay, between 2005 and 2011 as well as reduced

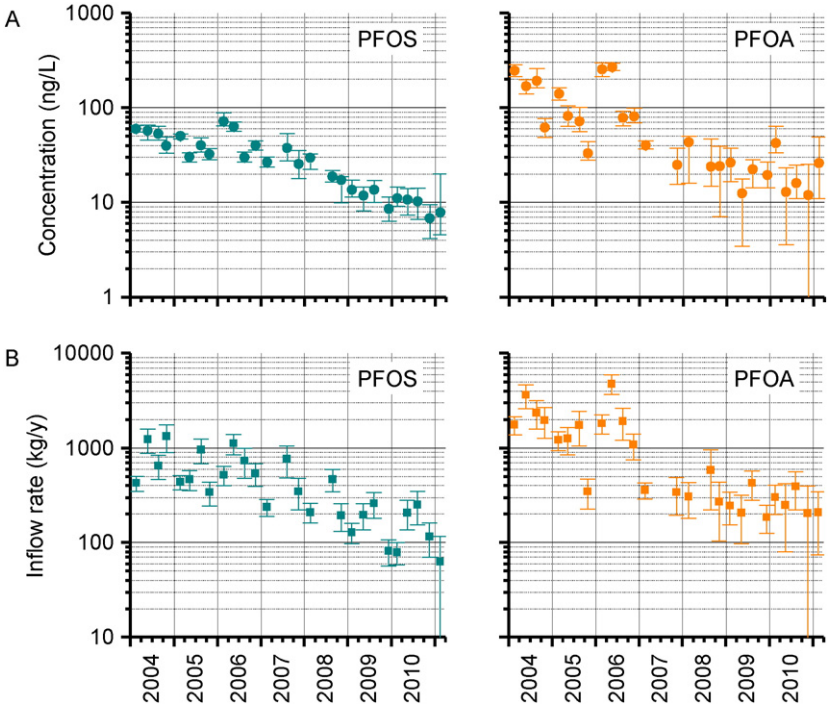

Fig. 3. Temporal trends of concentrations and inflow rates of PFOS and PFOA from February 2004 to February 2011. (A) Estimated average concentrations in freshwater flowing into Tokyo Bay. Error bars show 95% confidence intervals (CIs). (B) Estimated inflow rates to Tokyo Bay. Error bars show the estimated expanded uncertainty (coverage factor $k = 2$). Calculations for the period from February 2004 to February 2007 used data from 20 stations. Data were not available for PFOS in May 2007 and May 2008 or for PFOA in May and August 2007 and May 2008. An 87% CI is shown for the February 2008 sampling because the small number of salinity data precluded the calculation of a 95% CI.

Table 1
Average yearly inflow rates of PFOS and PFOA to Tokyo Bay.[a]

Year	Inflow rate (kg y^{-1})				Per-person inflow rate (μg d^{-1} $person^{-1}$)			
	PFOS		PFOA		PFOS		PFOA	
2004	910	(±150)	2400	(±380)	87	(±17)	230	(±43)
2005	550	(±83)	1100	(±210)	52	(±9.4)	110	(±23)
2006	730	(±110)	2400	(±360)	68	(±12)	230	(±41)
2007	450	(±80)	350	(±40)	42	(±8.2)	33	(±4.1)
2008	290	(±37)	390	(±110)	27	(±4.1)	36	(±10)
2009	170	(±27)	270	(±53)	15	(±2.9)	24	(±5.4)
2010	160	(±33)	290	(±82)	15	(±3.3)	26	(±7.8)

[a] Values in parentheses show estimated expanded uncertainty (coverage factor $k = 2$).

concentrations of PFOS and PFOA in the effluents of several WWTPs discharging to the river, which were attributed to reduced emissions from point industrial sources (Nishino et al., 2013). PFOS was designated as Class I Specified Chemical Substances under Japan's CSCL as of April 2010, and some factories may have phased out their use of PFOS, PFOA, and their precursors prior to the designation. Industries may also have reacted to regulations on these compounds in other countries (Zushi et al., 2012; Zushi et al., 2011).

Apart from the declining yearly trend, interpretation of the seasonal patterns for PFOS and PFOA and the differences between them are topics for future investigation. Assuming that emissions arise from industrial facilities and household use and arrive at the bay within several days of emission, the inflow rate to the bay should be independent of freshwater inflow rate and should not show a seasonal pattern, contrary to the observed trend for PFOS. Accumulation of these compounds on the way to the bay and subsequent flushing during high precipitation events could partially explain the observed seasonal pattern. If this is the case, differences in the location of major emission sources might explain the difference in seasonal pattern between the two compounds.

3.6. Comparison with previous emission estimates and contributions from point and diffuse sources

The inflow rates of these compounds to Tokyo Bay are comparable to or higher than their calculated flux through large rivers worldwide at the corresponding year of sampling (Yeung et al., 2009). Murakami et al. (2008) estimated sewage-derived fluxes of PFOS and PFOA as 3.6 t/y and 5.6 t/y, respectively, for the entire nation of Japan based on samples collected in 2005. Inflow rates of PFOS and PFOA to Tokyo Bay for 2005 were 550 kg/y and 1100 kg/y (Table 1), respectively, representing about 15% and 21% of the nationwide sewage-derived fluxes.

Our estimated I_{pp} values for PFOS were generally comparable to previously reported per-person waterborne emission rates in Europe (Becker et al., 2008; Huset et al., 2008; Pistocchi and Loos, 2009), the United States (Huset et al., 2008), Korea (Kim, 2012; Kim et al., 2014), and Japan (Murakami et al., 2008; Murakami et al., 2009; Zushi et al., 2011), whereas those for PFOA were generally higher than previously reported values (Tables 1 and 2). Interestingly, the average per-person emission rates for all of Japan, obtained by dividing estimates of sewage-derived flux of Murakami et al. (2008) by Japan's population, closely matched our per-person inflow values for that year in Tokyo Bay (Tables 1 and 2). We considered I_{pp} to be an approximation of the waterborne emission rate by assuming that 100% of the emitted compounds arrived at the bay within a time on the order of several days. We believe that the physico-chemical properties of PFOS and PFOA make these assumptions reasonable. However, PFOS and PFOA emitted through other forms, with solid waste for example, may take longer to reach the bay, and would be evaluated as inflow at a later time or even not at all in the framework of the present study. In addition, removal of PFOS and PFOA during water treatment processes was not considered because previous studies have not reported consistent results (Becker et al., 2008; Schultz et al., 2006; Sinclair and Kannan, 2006). These studies appear to share the same assumptions, and thus we considered it valid to compare our I_{pp} values with previously reported emission rates. In the present study, we chose population as a proxy of human activity in the catchment basin to normalize the inflow rate and to enable comparison among different regions, while recognizing that the emission of these compounds in the Tokyo Bay catchment basin was not strictly on a per-person basis (see discussion below).

Our method for estimating $\hat{C}_{FWI}$ based on measured concentrations in the receptor (Tokyo Bay) enabled us to comprehensively cover inflow to the bay, including inflow via direct discharge to the bay. Waterborne emission rates for PFOS and PFOA flowing into Tokyo Bay in 2004 that relied on measured concentrations in inflowing rivers were considerably underestimated (Odaka and Masunaga, 2006; Takazawa et al., 2009). The reason for this underestimation is unclear, but samples of river water may not have been representative of point emission sources. The higher inflow rates for PFOA than for PFOS found in the present study may reflect direct discharges from facilities on the coast (Zushi et al., 2011). This interpretation accords with the findings of Murakami et al. (2009) and Zushi et al. (2011), who reported PFOS

Table 2
Reported estimates of water-borne emission rates (μg d^{-1} $person^{-1}$) for PFOS and PFOA.

Year	PFOS	PFOA	Country	Area	Method[a]	Note[b]	Reference
2004	21	7.5	Japan	Tokyo Bay catchment basin	A	(i)	Odaka and Masunaga (2006)
2004	8.4	8.0	USA	Pacific Northwest	B	(ii)	Schultz et al. (2006)
2004	42	11	USA	Nationwide	B		Huset et al. (2008)
2004	13	–[c]	Japan	Tama River basin	A		Takazawa et al. (2009)
2004	7.4	–[c]	Japan	Tokyo Bay catchment basin	A, B	(i)	Takazawa et al. (2009)
2004	1.6	2.9	Japan	Tama River basin	A, B	(iii)	Takazawa et al. (2009)
2005	9.6	120	USA	NY State	B	(ii)	Sinclair and Kannan (2006)
2005	40	30	Germany	Bayreuth	B	(iv)	Becker et al. (2008)
2005	77	120	Japan	All Japan	B, C		Murakami et al. (2008)
2006	57	12	Switzerland	Glatt River basin	B		Huset et al. (2008)
2007	69	20	Japan	Tokyo Metropolis	B		Murakami et al. (2009)
2007	27	82	Europe	Europe	A		Pistocchi and Loos (2009)
2009	13	8.9	Japan	Tokyo Bay catchment basin	A	(i)	Zushi et al. (2011)
2010	30	26	Korea	Nationwide	B		Kim et al. (2014)
2010	2.0	2.4	Korea		B	(v)	Kim et al. (2014)

[a] A, measured concentration in rivers. B, measured concentration in wastewater treatment plant (WWTP) influent or effluent. C, estimated by using a sewage-marker compound.
[b] (i) The basin-wide emission rate reported in the original literature was divided by the effective population in the basin corresponding to the sampling dates (the effective population was calculated in the present study). (ii) Based on influent data. (iii) Domestic wastewater only, assuming one WWTP with the lowest emission rate to represent only domestic emissions. (iv) This study reported PFOS + PFOA emission rates of 1–3 μg/(d person) from household wastewater; higher emission rates from the Bayreuth WWTP were attributed to industrial and commercial wastewater. (v) >90% of the influent is wastewater produced from domestic human activities.
[c] Not reported.

emission rates comparable to our estimates but PFOA emission rates that were lower than our estimates, because their methods did not take into account such direct discharges to the bay. In addition, this interpretation accords with a study that suggested that point industrial emissions contribute to the PFOA emission rate in Europe (Pistocchi and Loos, 2009). Our method should be applicable to studies of inflow of other compounds that are similar to PFOS and PFOA in their physicochemical properties, including alternative perfluoroalkyl and polyfluoroalkyl acids.

A comparison with previous estimates of household emission rates of these compounds suggested that our inflow estimates included a considerable contribution from point industrial sources. Takazawa et al. (2009) suggested per-person household emission rates of 1.6 μg/d and 2.9 μg/d for PFOS and PFOA, respectively, based on the analysis of effluent samples collected from WWTPs in the Tama River basin in 2004 (Table 2). A similar range was reported on the basis of samples collected in 2005 for WWTPs in Germany that treated only household wastewater (1–3 μg/d for PFOS + PFOA) (Becker et al., 2008) and of samples collected in 2010 for WWTPs in South Korea that treated wastewater produced predominantly (>90%) from domestic human activities (PFOS, 2.0 μg/d; PFOA, 2.4 μg/d) (Kim et al., 2014). Our estimated values of I_{pp} (Table 1) for 2004 were about 50 times (PFOS) and 80 times (PFOA) the household emission rates suggested by Takazawa et al. (2009) in the Tama River basin. These higher values of I_{pp} can be attributed to contributions from emissions from point sources, urban surface runoff (Kim et al., 2014; Murakami et al., 2009; Zushi et al., 2008), and delayed emissions from accumulated PFOS and PFOA on their way to the bay.

3.7. Method validity and limitations

The mixing model of Eq. (1) relied on the following five assumptions: (a) salinity is conserved and PFOS and PFOA are not degraded in the bay; (b) the extent of mixing of PFOS and PFOA is similar to the extent of salinity mixing; (c) a single value C_{ocean} represents the concentration of PFOS or PFOA in the Pacific Ocean; (d) a single value C_{FWI} represents the concentration of PFOS or PFOA in various freshwater inflows; (e) the major sources of PFOS and PFOA in the samples are either freshwater inflow or Pacific Ocean water. Assumption (a) is sound considering the persistence of PFOS and PFOA in the environment. Assumption (b) is also sound because turbulent diffusion and advection would dominate the mixing of PFOS, PFOA, and salinity on the scale of the bay, which supports the use of S/S_{ocean} as α_{ocean}. Assumption (c) is reasonable considering the single and narrow connection between the bay and the Pacific Ocean, and the relatively low value of C_{ocean}. Assumption (d) is a key simplification in the model. Assumption (e) is supported in the following discussion.

An evaluation of the mass balance of PFOS and PFOA in the bay supported our focus on their waterborne transport to the bay and the use of the mixing model to estimate $\hat{C}_{FWI}$. The mass balance can be described as Eq. (7),

$$(dC)V = (dt)F \tag{7}$$

where V represents the volume of water in the bay, C is the concentration of PFOS or PFOA, t is time, and F represents the flux of PFOS or PFOA into and out of the bay.

The flux F can be divided into three components: flux via surface-water interface, flux via the atmospheric interface, and flux via the sediment interface (Eq. (8)).

$$F = F_{surface\text{-}water} + F_{atmosphere} + F_{sediment} \tag{8}$$

Flux via the surface-water interface includes $F_{surface\text{-}FWI}$ (via freshwater inflow) and F_{ocean} (via exchange of seawater at the bay's mouth). Flux via the sediment interface was neglected because we previously estimated it to be 2–3 orders of magnitude smaller than the flux via the surface-water interface (Sakurai et al., 2010). The effect of sediment resuspension was judged negligible because our previous results showed that the mass-basis concentrations of these compounds in suspended particles were roughly 70 to 80 times higher in the lower water layer than in sediment at the same station (Sakurai et al., 2010). Flux via the atmospheric interface was negligible based on the following considerations. On the basis of measurements made in 2006–2008 at two locations in the Kanto region of Japan (Kwok et al., 2010), the region including Tokyo Bay, wet deposition to the bay surface was estimated at 0.7 kg/y and 2 kg/y for PFOS and PFOA, respectively. Dry deposition was estimated at roughly 0.7 kg/y and 1 kg/y for PFOS and PFOA, respectively. The dry deposition values were obtained by multiplying airborne particulate concentrations of these compounds in other areas by a general settling velocity of airborne particles. The airborne concentrations were set at roughly 5 pg/m^3 (PFOS) and 2 pg/m^3 (PFOA) according to available measured values in air (Barber et al., 2007; Harada et al., 2005; Jahnke et al., 2007; Kim and Kannan, 2007) (note that the reported values were variable particularly for PFOA, and values measured on land were included), and the settling velocity was set at 1 cm/s as an order-of-magnitude estimate based on a wide range of reported values (Odabasi et al., 1999; Sakata et al., 2008; Slinn and Slinn, 1980). The resulting deposition fluxes for PFOS and PFOA were two or more orders of magnitude lower than those associated with freshwater inflow. Vapor evasion was estimated to be negligible owing to the negligibly low vapor pressure of the dissociated anion species (Barton et al., 2007), i.e., PFOS and PFOA, in the bay water with pH around or greater than 8 (Council of Local Governments for Tokyo Bay Environmental Preservation, 2012). In situ formation of PFOS and PFOA from precursors in the bay water was not considered because of a lack of reported data. These considerations were in agreement with previous mass balance analyses for perfluoroalkyl substances in Lake Ontario, USA/Canada (Boulanger et al., 2005), and urban lakes in Albany, NY, USA (Kim and Kannan, 2007).

The above consideration reduces Eq. (8) to Eq. (9),

$$F \approx F_{surface\text{-}water} + F_{precipitation} = F_{FWI} + F_{ocean} \tag{9}$$

where freshwater inflow (FWI) represents surface freshwater inflow plus precipitation on the bay surface. Wet deposition ($F_{precipitation}$, inflow due to precipitation) to the bay surface was included in Eq. (9) because subsequent analysis of freshwater inflows did not distinguish precipitation on the bay surface from other surface inflows.

By taking into account both pathways of input, the mass of PFOS or PFOA in a small volume (ΔV) of bay water can be described by Eq. (10), which leads to the mixing model of Eq. (1).

$$C\Delta V = \alpha_{FWI} C_{FWI} \Delta V + \alpha_{ocean} C_{ocean} \Delta V \tag{10}$$

where α represents the relative contribution of each input pathway ($\alpha_{FWI} + \alpha_{ocean} = 1$) in ΔV.

In estimating $\hat{C}_{FWI}$, we used values from the literature for C_{ocean} considering the relatively small number of samples (≤8) in the sampling campaigns after February 2007 and the observed variability in the data. The WLS regression failed to give statistically significant results in 8 of the 53 regressions. In the present study, $\hat{C}^{-2}$, instead of the previously used C^{-2} (Sakurai et al., 2010), was used as a weight in the WLS regression, because we considered the former to give more reasonable estimates. We supposed that the duration of each sampling campaign was sufficiently short in terms of changes in the average concentrations of these compounds in the freshwater inflow and changes in their concentrations in the bay water, and that the C_{FWI} values obtained from a sampling campaign thus were distributed over a relatively narrow range. The range of estimated $\hat{C}_{FWI}$ values (PFOS, 6.8–72 ng/L; PFOA, 12–270 ng/L) was in accordance with reported concentrations of PFOS

and PFOA in rivers and WWTP effluents in the basin (Murakami et al., 2008; Murakami et al., 2009; Sakurai et al., 2010; Takazawa et al., 2009; Zushi et al., 2011). We reported $\hat{C}_{FWI}$ values corresponding to zero salinity because it was not practical to assign a representative value of salinity in freshwater inflow (S_{FWI}) other than zero and because we believe that the average salinity in freshwater inflows is low compared to that in ocean water, although the freshwater considered in the present study might have high salinity in some industrial effluents.

The system of water flow in the Tokyo-Bay catchment basin is a complicated set of networks of rivers, water supply systems, and wastewater effluent systems, covering multiple river basins (Okada et al., 2007), and these networks were carefully considered in the present study. The networks serve the water demands of a concentrated population, control flooding in and around the basin (Miyamura, 1993; Okada et al., 2007), and have historically provided an efficient means for river navigation. Okada et al. (2007) is the most recent comprehensive study of freshwater inflow to Tokyo Bay that updated previous few studies and provided the basis for the present study. That study estimated the rate of freshwater inflow to Tokyo Bay on the basis of precipitation to the catchment basin, precipitation to the bay surface, and import of water from outside the catchment basin. In estimating $\hat{q}_{FWI}$ and $\hat{N}_e$, we assumed the same time course of weather, particularly precipitation events, over the catchment basin of the bay. Because we considered precipitation to be the primary source of freshwater inflow, this assumption led to the use of a simple linear form to estimate $\hat{q}_{FWI}$ and the omission of the intercept term in Eq. (6) (SM Fig. S5). This assumption was acceptable because the basin is located in a region surrounded by the Pacific Ocean to the east and south and mountainous areas to the west and north (Fig. 2). We chose the flow rate of the Tone River at the Tone-Ohzeki diversion weir to estimate $\hat{q}_{FWI}$ because of the availability of data for the study period and because we judged that q_{TR}, without upstream water intake out of the river basin, represents precipitation that basically determines the freshwater inflow to the bay. The time required for the precipitation to reach rivers, the time for a weather event to cross the basin, and differences in weather in different parts of the basin were not considered. The time for waterborne emission in the bay's basin to reach the bay was considered to be on the order of several days (Ono and Morita, 1976; Yanase, 1976).

3.8. Uncertainty analysis of the inflow estimates

The relative expanded uncertainty in the inflow rate, $E(I_{basin})$, ranged from 0.18 to 0.87 (median 0.29) for PFOS and from 0.19 to 0.95 (median 0.36) for PFOA among the sampling campaigns (Fig. 3B). $E(I_{pp})$ was larger than $E(I_{basin})$ because it included the uncertainty in the estimated effective population in the Tokyo Bay catchment basin ($\varepsilon(\hat{N}_e)$) (Eq. (5)), and it ranged from 0.22 to 0.87 (median 0.35) for PFOS and from 0.23 to 0.97 (median 0.40) for PFOA (SM Figs. S8 and S9). $\varepsilon(\hat{C}_{FWI})$ varied among the sampling campaigns, and after February 2007 it was the largest contributor to the relative uncertainty of most of the estimated I_{basin} and I_{pp} values for PFOS and all of those for PFOA. $\varepsilon(\hat{q}_{FWI})$ and $\varepsilon(\hat{N}_e)$ were relatively constant among the sampling campaigns. Some relatively high $\varepsilon(\hat{q}_{FWI})$ values (around 15%) resulted partly from high flow rates (>1000 m^3/s in the Tone River) during the averaging period before the sampling dates. The uncertainty in weights ($w(k)$, Eq. (4)) accounted for the major part of $\varepsilon(\hat{N}_e)$, which appears high for the population data based on the censuses.

The estimated uncertainties associated with the inflow rates of these compounds validated our discussion of the temporal trends of the inflow rates and their comparison with previously reported emission rates. $\varepsilon(\hat{C}_{FWI})$, which was the largest contributor to the relatively high uncertainties associated with some estimates of the inflow rates, may be reduced by increasing the number of sampling points, as shown by the smaller values obtained from the 20-station data (Figs. 3A and SM Figs. S8 and S9). Conducting several sampling campaigns during the timeframe of the residence time of water in Tokyo Bay (Okada et al., 2007) would lead to more representative estimates of $\hat{C}_{FWI}$ and its variability. The obtained expanded uncertainty does not include the uncertainty in selecting models such as Eqs. (1), (3), (4), and (6). We proposed these models as the best available representation of reality given limited information.

4. Conclusions

A combination of seasonal sampling campaigns and chemical, statistical, hydrological, and demographic analysis enabled us to base the estimation of $\hat{C}_{FWI}$ on the changing seawater structure of the bay (Sakurai et al., 2010), to relate seasonal changes in $\hat{q}_{FWI}$ to inflow estimates, and to demonstrate temporal trends for the inflow of PFOS and PFOA over the period from February 2004 to February 2011.

The considerable reduction in the inflow rates of PFOS and PFOA to Tokyo Bay during the study period probably reflected a reduction in the use and emission of these compounds and their precursors in the Tokyo Bay catchment basin. The inflow rates of these compounds to Tokyo Bay were higher or comparable to their calculated flux through large rivers elsewhere at the same times (Yeung et al., 2009). Our estimated per-person inflow rates for PFOS were generally comparable to previously reported per-person waterborne emission rates in Japan and other countries, whereas those for PFOA were generally higher than previously reported per-person waterborne emission rates. Our method for estimating $\hat{C}_{FWI}$ based on measured concentrations in the receptor (Tokyo Bay) enabled us to comprehensively cover inflow to the bay, including inflow via direct discharge to the bay. A comparison with previous estimates of household emission rates of these compounds suggested that our inflow estimates included a large contribution from point industrial sources. The estimated uncertainties associated with the inflow rates of these compounds validated our discussion of the temporal trends of inflow rates and their comparison with previously reported emission rates.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

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References

Ankley, G.T., Kuehl, D.W., Kahl, M.D., Jensen, K.M., Butterworth, B.C., Nichols, J.W., 2004. Partial life-cycle toxicity and bioconcentration modeling of perfluorooctanesulfonate in the northern leopard frog (*Rana pipiens*). Environ. Toxicol. Chem. 23, 2745–2755.

Barber, J.L., Berger, U., Chaemfa, C., Huber, S., Jahnke, A., Temme, C., et al., 2007. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. J. Environ. Monit. 9, 530–541.

Barton, C.A., Kaiser, M.A., Russell, M.H., 2007. Partitioning and removal of perfluorooctanoate during rain events: the importance of physical-chemical properties. J. Environ. Monit. 9, 839–846.

Becker, A.M., Gerstmann, S., Frank, H., 2008. Perfluorooctane surfactants in waste waters, the major source of river pollution. Chemosphere 72, 115–121.

Boulanger, B., Peck, A.M., Schnoor, J.L., Hornbuckle, K.C., 2005. Mass budget of perfluorooctane surfactants in Lake Ontario. Environmental Science & Technology 39, 74–79.
Council of Local Governments for Tokyo Bay Environmental Preservation. Report of Water Quality in Tokyo Bay (FY 2010), 2012. (in Japanese).
Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environmental Science & Technology 35, 1339–1342.
Giesy, J.P., Kannan, K., 2002. Perfluorochemical surfactants in the environment. Environmental Science & Technology 36, 146A–152A.
Harada, K., Nakanishi, S., Saito, N., Tsutsui, T., Koizumi, A., 2005. Airborne perfluorooctanoate may be a substantial source contamination in Kyoto Area, Japan. Bull. Environ. Contam. Toxicol. 74, 64–69.
Hekster, F.M., Laane, R.W.P.M., de Voogt, P., 2003. Environmental and toxicity effects of perfluoroalkylated substances. In: Ware, G. (Ed.), Reviews of Environmental Contamination and Toxicology, 179 179. Springer-Verlag, New York, pp. 99–121.
Hoff, R.M., 1994. An error budget for the determination of the atmospheric mass loading of toxic chemicals in the Great Lakes. J. Great Lakes Res. 20, 229–239.
Hollander, M., Wolfe, D.A., 1999. Nonparametric Statistical Methods. New York, USA, John Wiley & Sons, Inc.
Houde, M., De Silva, A.O., Muir, D.C.G., Letcher, R.J., 2011. Monitoring of perfluorinated compounds in aquatic biota: an updated review. Environmental Science & Technology 45, 7962–7973.
Huset, C.A., Chiaia, A.C., Barofsky, D.F., Jonkers, N., Kohler, H.-P.E., Ort, C., et al., 2008. Occurrence and mass flows of fluorochemicals in the Glatt Valley watershed, Switzerland. Environmental Science & Technology 42, 6369–6377.
Jahnke, A., Berger, U., Ebinghaus, R., Temme, C., 2007. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53° N − 33° S). Environmental Science & Technology 41, 3055–3061.
Joint Committee for Guides in Metrology. Guides to the expression of uncertainty in measurement. JCGM 100:2008.
Kim, S.-K., 2012. Watershed-based riverine discharge loads and emission factor of perfluorinated surfactants in Korean peninsula. Chemosphere 89, 995–1002.
Kim, S.-K., Kannan, K., 2007. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes. Environmental Science & Technology 41, 8328–8334.
Kim, S.-K., Li, D.-H., Shoeib, M., Zoh, K.-D., 2014. Contribution of diffuse inputs to the aqueous mass load of perfluoroalkyl acids in river and stream catchments in Korea. Sci. Total Environ. 470–471, 1430–1440.
Kwok, K.Y., Taniyasu, S., Yeung, L.W.Y., Murphy, M.B., Lam, P.K.S., Horii, Y., et al., 2010. Flux of perfluorinated chemicals through wet deposition in Japan, the United States, and several other countries. Environmental Science & Technology 44, 7043–7049.
Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., Seed, J., 2007. Perfluoroalkyl acids: a review of monitoring and toxicological findings. Toxicol. Sci. 99, 366–394.
Ministry of Land, Infrastructure and Transport, 2007. River Discharge Year Book of Japan (Year 2003). Year 2003, Vol. 56. Japan River Association, Tokyo.
Miyamura, T., 1993. Waters flowing into Tokyo Bay. In: Kaizuka, S. (Ed.), Topography, Geology and Hydrology of Tokyo Bay. Tsukiji Shokan Publishing, Tokyo, Japan, pp. 111–134 (in Japanese).
Murakami, M., Imamura, E., Shinohara, H., Kiri, K., Muramatsu, Y., Harada, A., et al., 2008. Occurrence and sources of perfluorinated surfactants in rivers in Japan. Environmental Science & Technology 42, 6566–6572.
Murakami, M., Shinohara, H., Takada, H., 2009. Evaluation of wastewater and street runoff as sources of perfluorinated surfactants (PFSs). Chemosphere 74, 487–493.
Nishino, T., Ueno, K., Takahashi, A., Takazawa, Y., Shibata, Y., Nakama, S., et al., 2013. Perfluorinated compounds in Tamagawa River basin—trend of contamination and mass flow. Journal of Environmental Chemistry 23, 177–186 (in Japanese).
Odabasi, M., Sofuoglu, A., Vardar, N., Tasdemir, Y., Holsen, T.M., 1999. Measurement of dry deposition and air–water exchange of polycyclic aromatic hydrocarbons with the water surface sampler. Environmental Science & Technology 33, 426–434.
Odaka, R., Masunaga, S., 2006. Environmental behavior of perfluorinated surfactants in Tokyo Bay. Journal of Japan Society on Water Environment 29, 221–228 (in Japanese).
Okada, T., Takao, T., Nakayama, K., Furukawa, K., 2007. Change in freshwater discharge and residence time of seawater in Tokyo Bay. Journal of Hydraulic, Coastal and Environmental Engineering 63, 67–72 (in Japanese).
Olsen, G.W., Burris, J.M., Ehresman, D.J., Froehlich, J.W., Seacat, A.M., Butenhoff, J.L., et al., 2007. Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers. Environ. Health Perspect. 115, 1298–1305.
Ono, H., Morita, S., 1976. A record of time course and countermeasures of a water quality incident at the water sources for public water supply. Journal of Japan Water Works Association. 506, 114–124 (in Japanese).
Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environmental Science & Technology 43, 386–392.
Pistocchi, A., Loos, R., 2009. A map of European emissions and concentrations of PFOS and PFOA. Environmental Science & Technology 43, 9237–9244.
Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environmental Science & Technology 40, 32–44.
Sakata, M., Tani, Y., Takagi, T., 2008. Wet and dry deposition fluxes of trace elements in Tokyo Bay. Atmos. Environ. 42, 5913–5922.
Sakurai, T., Kim, J.G., Suzuki, N., Matsuo, T., Li, D.Q., Yao, Y.A., et al., 2000. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediment, soil, fish, shellfish and crab samples from Tokyo Bay area, Japan. Chemosphere 40, 627–640.
Sakurai, T., Kobayashi, J., Kinoshita, K., Ito, N., Serizawa, S., Shiraishi, H., et al., 2013. Transfer kinetics of perfluorooctane sulfonate from water and sediment to a marine benthic fish, the marbled flounder (*Pseudopleuronectes yokohamae*). Environ. Toxicol. Chem. 32, 2009–2017.
Sakurai, T., Serizawa, S., Isobe, T., Kobayashi, J., Kodama, K., Kume, G., et al., 2010. Spatial, phase, and temporal distributions of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in Tokyo Bay, Japan. Environmental Science & Technology 44, 4110–4115.
Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F., Field, J.A., 2006. Fluorochemical mass flows in a municipal wastewater treatment facility. Environmental Science & Technology 40, 7350–7357.
Sinclair, E., Kannan, K., 2006. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environmental Science & Technology 40, 1408–1414.
Slinn, S.A., Slinn, W.G.N., 1980. Predictions for particle deposition on natural waters. Atmospheric Environment (1967) 14, 1013–1016.
Suzuki, N., Murasawa, K., Nansai, K., Sakural, T., Matsuhashi, K., Moriguchi, Y., et al., 2005. Development of geo-referenced environmental fate model (G-CIEMS) for chemical contaminants based on GIS (geographic information system). Journal of Environmental Chemistry 15, 385–395 (in Japanese).
Suzuki, N., Murasawa, K., Sakurai, T., Nansai, K., Matsuhashi, K., Moriguchi, Y., et al., 2004. Geo-referenced multimedia environmental fate model (G-CIEMS): model formulation and comparison to the generic model and monitoring approaches. Environmental Science & Technology 38, 5682–5693.
Takazawa, Y., Nishino, T., Sasaki, Y., Yamashita, H., Suzuki, N., Tanabe, K., et al., 2009. Occurrence and distribution of perfluorooctane sulfonate and perfluorooctanoic acid in the rivers of Tokyo. Water Air Soil Pollut. 202, 57–67.
U.S. Environmental Protection Agency. 2010/2015 PFOA Stewardship Program. Washington DC; 2006 [http://www.epa.gov/opptintr/pfoa/pubs/stewardship/index.html (accessed 04 June 2014)].
Nations, U., 2009. Adoption of Amendments to Annexes A, B and C of Stockholm Convention on Persistent Organic Pollutants (Stockholm, 22 May 2001).
Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A global survey of perfluorinated acids in oceans. Mar. Pollut. Bull. 51, 658–668.
Yanase, A., 1976. Phenol spill incident in the Tone River—time course and countermeasures. J. Jpn. Water Works Assoc. 506, 91–100 (in Japanese).
Yeung, L.W.Y., Yamashita, N., Taniyasu, S., Lam, P.K.S., Sinha, R.K., Borole, D.V., et al., 2009. A survey of perfluorinated compounds in surface water and biota including dolphins from the Ganges River and in other waterbodies in India. Chemosphere 76, 55–62.
Zushi, Y., Hogarh, J., Masunaga, S., 2012. Progress and perspective of perfluorinated compound risk assessment and management in various countries and institutes. Clean Techn. Environ. Policy 14, 9–20.
Zushi, Y., Takeda, T., Masunaga, S., 2008. Existence of nonpoint source of perfluorinated compounds and their loads in the Tsurumi River basin, Japan. Chemosphere 71, 1566–1573.
Zushi, Y., Ye, F., Motegi, M., Nojiri, K., Hosono, S., Suzuki, T., et al., 2011. Spatially detailed survey on pollution by multiple perfluorinated compounds in the Tokyo Bay basin of Japan. Environmental Science & Technology 45, 2887–2893.